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INVESTMENT CASTING OF BULK-SOLIDIFYING AMORPHOUS  
ALLOYS AND ARTICLES MADE THEREOF

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FIELD OF THE INVENTION

The present invention relates to casting of bulk-solidifying amorphous alloys, and more particularly to investment casting of bulk-solidifying amorphous alloys and articles of bulk solidifying amorphous alloys made using such investment casting methods.

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BACKGROUND OF THE INVENTION

Bulk-solidifying amorphous alloys are a recently discovered family of amorphous alloys, which can be cooled at substantially lower cooling rates, of about 500 K/sec or less, than conventional amorphous alloys while still retaining their amorphous atomic structure. As a result of this reduced cooling rate, these bulk-solidifying amorphous alloys can be produced in thicknesses of 1.0 mm or more, substantially thicker than conventional amorphous alloys, which require cooling rates of  $10^5$  K/sec or more, and which can only be cast in thicknesses of about 0.020 mm. U.S. Patent Nos. 5,288,344; 5,368,659; 5,618,359; and 5,735,975 (the disclosures of which are incorporated herein by reference) disclose such bulk-solidifying amorphous alloys.

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Articles made from such bulk-solidifying amorphous alloys are generally produced by permanent mold casting, and more specifically in processes which utilize metallic molds. For example, U.S. Patent Nos. 6,021,840 and 5,711,363 (the disclosures of which are incorporated herein by reference) describe such methods utilizing die-casting techniques. In the die-casting process a molten feedstock of a bulk-solidifying amorphous alloy composition is cast into a metallic mold cavity. In such a method the metallic mold mass provides the rapid cooling necessary to form the amorphous phase during solidification.

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Generally, permanent mold casting is preferred over other techniques when using bulk-solidifying amorphous alloys because this method provides a relatively high cooling rate and a high production rate. However, there are cases where permanent mold casting has certain shortcomings and, as a result, cannot be generally applied. For example, a metallic mold needs to be machined to produce shaped articles of bulk-solidifying amorphous alloys. Machining such molds is not only time-consuming, but requires a substantial financial investment in order to address the various complexities in permanent mold casting. Furthermore, even slight changes in the geometry of the mold cavity may cause major difficulties and, as such, even subtle subsequent design changes generally require machining new molds causing lost time and increased costs. These shortcomings becomes particularly acute in developing new products and prototypes, and in cases where one-of-a-kind or small runs are desired. As such, machining a new mold for each shape becomes a cost-prohibitive factor and hinders the market penetration of bulk-solidifying amorphous alloys to the rapid developments in design change.

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Another potential shortcoming of permanent mold casting is the detailed replication of mold features. As the molten feedstock is fed into the mold cavity, rapid cooling takes place, which accelerates solidification and impedes the flow of the viscous fluid into the intricate details of the mold cavity. The relatively cold surface of the mold cavity and the high thermal conductivity of the metallic mold material precludes any wetting of the molten alloy to the mold surface. This matter is especially pronounced in thin sections where the thickness of the article is less than about 2.0 mm.

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Accordingly, a need exists for an improved casting method for bulk-solidifying amorphous alloys, which will allow for low cost tooling, and should allow rapid implementation of design changes and complete replication of mold features, while still allowing for the formation of articles having the desired amorphous phase properties.

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## SUMMARY OF THE INVENTION

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The current invention is directed to a method of investment casting bulk-solidifying amorphous alloys, and the formation of articles of bulk-solidifying amorphous alloys made by such methods.

## BRIEF DESCRIPTION OF THE DRAWINGS

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These and other features and advantages of the present invention will become appreciated as the same becomes better understood with reference to the specification, claims and drawings wherein:

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FIG. 1, is a flow diagram of a conventional method of forming molded articles of conventional alloys using investment casting;

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FIG. 2, is a flow diagram of a method of forming molded articles of bulk-solidifying amorphous alloys according to the present invention using investment casting; and

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FIG. 3a, is a graphical depiction of the solidification properties of bulk amorphous alloys according to the present invention.

FIG. 3b, is a graphical depiction of the solidification properties of bulk amorphous alloys according to the present invention.

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FIG. 4, is a graphical representation of the phase change properties of an exemplary embodiment of the bulk-solidifying amorphous alloys according to the present invention.

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FIG. 5, is a graphical representation of the crystallization properties of an exemplary embodiment of the bulk-solidifying amorphous alloys according to the present invention.

FIG. 6, is a graphical representation of the crystallization properties of another exemplary embodiment of the bulk-solidifying amorphous alloys according to the present invention.

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## DETAILED DESCRIPTION OF THE INVENTION

The current invention is directed to a method of investment casting bulk-solidifying amorphous alloys, and the formation of articles of bulk-solidifying amorphous alloys made by such methods.

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Investment casting is a generally well established method for processing conventional metallic alloys. The general steps of investment casting are described in reference to the flow-chart shown in Figure 1. First, a wax pattern is produced which imitates the shape of the desired final component. (Step 1) Several of these wax patterns can be attached into a wax tree having a suitable network of gates and sprues to cast multiple parts at a time.

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The wax pattern is then dipped into a suitable slurry bath and a coating is formed around the wax pattern. (Step 2)

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The coated slurry is then dried to form a rigid shell around the wax pattern. (Step 3) This step can be repeated several times to provide a sufficiently rigid and strong shell, which will act as a mold. (Optional Step 3a) In this step the composition and type of the slurry used can be varied in each coating step to provide optimum surface finish, strength, and rigidity. In an alternative embodiment, the investment shell can be prepared by quicker methods, such as by casting a pre-mixed slurry around the wax pattern, or alternatively, by submerging the wax pattern into a suitably sized slurry bath and letting the slurry bath solidify around the wax pattern.

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The wax is then melted and burned out to leave a clean investment shell with cavities having the shape of the desired components and gates and sprues for multiple cavity patterns. (Step 4)

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Then, the molten metal is introduced into the investment shell and left to solidify to form the shape of the cavities. (Step 5) In this step it is a common practice to heat the investment shell to elevated temperatures (however, below the melting temperature of the metal and alloy) to delay the solidification of the metal and, as such, improve the fluidity of the melt and ultimately allow for more complete filling of the investment shell cavity.

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Subsequent to the solidification, the investment shell is separated from the cast metal components by agitation or other mechanical methods. (Step 6) During this step the investment shell is destroyed and as such investment casting process, in principle, one mold is used for each cast component.

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Further, post-cast finishing processes may be employed to finish the cast components such as, for example, cleaning the surface from any reaction and/or residue remaining from the investment mold.

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In such conventional investment casting processes, the molten metal is cooled rather slowly. This is necessary in order to preserve the fluidity of the molten metal longer and to reduce the accumulation of any thermal stresses. Since it is generally desired to avoid superheating of the molten metal above its melting temperature, in order to avoid coarse and inferior grain-structure, the effect of the slow cooling rate of this method in improving the fluidity of the melt is crucial. Further, this conventional investment casting is generally carried out when more precise and intricate parts are desired and, as such, quenching during the investment casting is not desired as it will cause thermal stresses and distortions in those parts. Indeed, the high solidification shrinkage of conventional metals during solidification often causes the breakage of parts during fast cooling of such intricate articles. In addition, thermal shock and high thermal stresses may also cause the investment shell to breaks and loose its integrity.

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Accordingly, the prior art of investment casting is geared towards slow cooling of the molten metal rather than fast cooling or quenching. As a result,

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heating of the investment shell to elevated temperatures and the use of thick  
investment shells (up to 10 mm or more) are commonly practiced to subdue  
5 the cooling rate during the investment casting process.

Bulk-solidifying amorphous alloys are a recently discovered family of  
amorphous alloys, which can be cooled at substantially lower cooling rates, of  
about 500 K/sec or less, than conventional alloys, while still retaining their  
10 amorphous atomic structure. As such, these alloys can be produced in  
thicknesses of 1.0 mm or more, substantially thicker than conventional  
amorphous alloys, which are typically limited to articles having thicknesses of  
about 0.020 mm, and which require cooling rates of  $10^5$  K/sec or more. U.S.  
15 Patent Nos. 5,288,344; 5,368,659; 5,618,359; and 5,735,975 (the disclosures o  
which are incorporated herein by reference) disclose such bulk-solidifying  
amorphous alloys.

Although any bulk-solidifying amorphous alloys can be used in the  
20 present invention, one exemplary family of bulk-solidifying amorphous alloys  
can be described by the molecular formula  $(\text{Zr,Ti})_a(\text{Ni,Cu, Fe})_b(\text{Be,Al,Si,B})_c$ ,  
where a is in the range of from about 30 to 75, b is in the range of from about  
5 to 60, and c in the range of from about 0 to 50 in atomic percentages.  
25 Furthermore, these alloys can accommodate substantial amounts of other  
transition metals up to about 20 % atomic, and more. Although any  
transition metal may be included, preferably these metals include Nb, Cr, V,  
and Co. For example, a preferred alloy family is  $(\text{Zr,Ti})_a(\text{Ni,Cu})_b(\text{Be})_c$ , where a  
30 is in the range of from about 40 to 75, b is in the range of from about 5 to 50,  
and c in the range of from about 5 to 50 in atomic percentages. Still, a more  
preferred composition is  $(\text{Zr,Ti})_a(\text{Ni,Cu})_b(\text{Be})_c$ , where a is in the range of from  
about 45 to 65, b is in the range of from about 7.5 to 35, and c in the range of  
35 from about 10 to 37.5 in atomic percentages. Finally, another preferred alloy  
family is  $(\text{Zr})_a(\text{Nb,Ti})_b(\text{Ni,Cu})_c(\text{Al})_d$ , where a is in the range of from about 45 to

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65, b is in the range of from 0 to 10, c is in the range of from about 20 to 40  
and d in the range of from about 7.5 to 15 in atomic percentages.

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These Zr-based bulk-solidifying amorphous alloys can sustain strains  
up to about 1.5 % or more and generally around about 1.8 % without any  
permanent deformation or breakage. Further, they have high fracture  
toughness of about 10 ksi-sqrt(in) (sqrt: square root) or more, and preferably  
10 about 20 ksi sqrt(in) or more. Also, these alloys have high hardness values of  
about 4 GPa or more, and preferably about 5.5 GPa or more. The yield  
strength of these bulk solidifying alloys range from about 1.6 GPa and reach  
up to about 2 GPa and more, exceeding the current state of titanium-based  
15 alloys.

Another set of bulk-solidifying amorphous alloys are compositions  
based on ferrous metals (Fe, Ni, Co). Examples of such compositions are  
disclosed in U.S. Patent No. 6,325,868, (A. Inoue et. al., Appl. Phys. Lett.,  
20 Volume 71, p 464 (1997)), (Shen et. al., Mater. Trans., JIM, Volume 42, p 2136  
(2001)), and Japanese patent application 2000126277 (Publ. # .2001303218  
A). (The disclosures of which are incorporated herein by reference.) One  
exemplary composition of such alloys is  $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ . Another  
25 exemplary composition of such alloys is  $\text{Fe}_{72}\text{Al}_7\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ . Although, these  
alloy compositions are not processable to the degree of the Zr-base alloy  
systems, they can still be processed in thicknesses of around 1.0 mm or more,  
which is sufficient to be utilized in specific embodiments of the current  
invention. Similarly, these alloys have elastic strain limits of higher than  
30 about 1.2 %, and generally around about 1.8 %. The yield strength of these  
ferrous-based bulk-solidifying amorphous alloys is also higher, ranging from  
about 2.5 GPa to about 4 GPa or more, making them particularly attractive.  
Ferrous metal-base bulk amorphous alloys also very high yield hardness  
35 ranging from about 7.5 GPa to about 12 GPa.

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Although relatively pure amorphous phase bulk-solidifying amorphous alloys are discussed above, it is possible to use bulk-solidifying amorphous alloys including crystalline precipitates in the current invention. In general, crystalline precipitates in bulk-solidifying amorphous alloys are highly detrimental to their properties, especially to the toughness and strength of such alloys, and, as such, it is generally preferred to keep these precipitates to as small a volume fraction as possible. However, there are ductile crystalline phases, which precipitate in-situ during the processing of bulk-solidifying amorphous alloys, which are indeed beneficial to the properties of bulk-solidifying amorphous alloys, and particularly to the toughness and ductility of such alloys. Such bulk-solidifying amorphous alloys comprising such beneficial precipitates are also included in the current invention. One exemplary case is disclosed in (C.C. Hays et. al, Physical Review Letters, Vol. 84, p 2901, 2000) (the disclosure of which is incorporated herein by reference). This alloy has an elastic strain limit of about 1.8% or more and a yield strength of about 1.4 GPa and more, depending on the specific microstructure of the crystalline precipitates.

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The investment casting process has not yet been successfully applied to the production of these bulk-solidifying amorphous alloys. The main issue with the adaptation of investment casting to the production of bulk-solidification amorphous alloys is the ability to employ sufficient cooling rates from the melting temperatures of bulk-solidifying amorphous alloys to down below the glass transition temperatures of bulk-solidifying amorphous alloys. Another significant issue is the reaction of the molten alloy with the investment mold or residues left behind in the investment mold. Further, the relatively porous structure of the investment mold hinders the release of reactive gases (such as oxygen, moisture) from the mold surface, which subsequently reacts with molten alloy and degrades the surface finish of the metallic cast components. These last two issues become especially prominent



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with reactive bulk-solidifying amorphous alloys and compositions sensitive to  
oxidation such as in the case of Zr-Ti base alloys.

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The current invention is directed to novel methods to apply the  
investment casting process suitably to the production of bulk-solidifying  
amorphous alloys and methods to identify bulk-solidifying amorphous alloys  
suitable for such investment casting.

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The main steps of investment casting of bulk solidifying amorphous  
alloys are shown in the flow-chart provided in Figure 2, and provided in the  
following list:

- 15  
1) Providing a suitable investment mold having a cavity (or cavities)  
with the shape of the desired component(s) (Step 1);
- 2) Providing a feedstock of bulk solidifying amorphous alloy (Step 2);
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3) Heating the feedstock of the alloy above the melting temperature  
(Step 3);
- 4) Introducing the molten alloy into the cavity of the investment mold  
and filling of the cavities of the investment mold with the molten  
bulk-solidifying amorphous alloy (Step 4);
- 25  
5) Bringing the filled investment mold into contact with a quenching  
medium (Step 5);
- 6) Separating the investment mold from the metallic cast component  
(Step 6);
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7) (Optional) Keeping the metallic cast component in contact with a  
quenching medium until the whole part is cooled to well-below glass  
transition temperature (Step 7).

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As shown in Figure 2, and described above, there are several additional  
steps and considerations in the investment casting of bulk-solidifying  
amorphous alloys. First, in Step 3, the provided feedstock of bulk-solidifying

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amorphous alloy is heated above the melting temperature, and preferable  
with a substantial superheating. It should be noted that the initial feedstock  
5 material does not need to have an amorphous phase.

In one preferred embodiment, superheating the feedstock to about 100  
°C above the melting temperature is utilized. In another embodiment,  
superheating to about 200 °C or more is employed. Such superheating is  
10 generally not detrimental to the physical properties of bulk-solidifying  
amorphous alloys (unlike conventional crystalline metals) and can  
substantially enhance the fluidity of the alloy and improve cavity-filling,  
precluding a need for heating the investment shell to elevated temperatures.  
15 However, in cases where heat extraction is limited, or a larger amount of heat  
needs to be extracted due to overall part dimensions, superheating can be  
decreased to obtain a sufficient cooling rate to form the amorphous phase.

In conventional investment casting, the investment shell is preferably  
20 heated up to substantially elevated temperatures. As shown in Step 4, this is  
not necessarily preferred for investment casting of bulk-solidifying amorphous  
alloys. For example, in order to enhance the cooling rate, the heating of the  
investment shell is preferred to have a thickness of about 5.0 mm or lower,  
25 and more preferably 3.0 mm or lower. Even though, heating the investment  
shell can aid the release of trapped gas and humidity just before the  
introduction of molten metal, the heating of the investment shell should be  
limited to temperatures around the glass transition rather than close to the  
30 melting temperatures of these alloys. This becomes particularly important for  
the case of Zr-Ti based alloys, which may react with the investment shell and  
degrade the surface quality of the casting. To prevent this preferably the  
heating of the bulk amorphous metal is carried out under inert atmosphere or  
35 partial vacuum or full vacuum.

A surprising benefit of using such bulk-solidifying amorphous alloys is  
that they solidify rather gradually in a continuous manner unlike

1 conventional metals which solidify in a discontinuous manner. This is  
illustrated graphically by FIGs. 3a and 3b which show the change in viscosity  
5 and volume, respectively, of a bulk-solidifying amorphous alloy as it solidifies.  
As detailed in the Figures, bulk-solidifying amorphous alloys retain their  
fluidity from above the melting temperature down to the glass transition  
temperature due to the lack of a first order phase transition. This is in direct  
10 contrast conventional metals and alloys. Since, bulk amorphous alloys retain  
their fluidity they do not accumulate significant stress from their casting  
temperatures down to below the glass transition temperature in the  
investment mold, and as such the premature cracking of the investment mold  
15 is avoided. Indeed, the cracking of the investment shell is preferred after the  
temperature of the outer portion of the cast part is reduced to temperatures  
below glass transition temperature in order to aid the cooling rate.  
Accordingly, the investment mold does not need to be heated to elevated  
20 temperatures as in the investment casting procedure of conventional alloys.  
This allows the use of a faster quenching rate than is possible in a typical  
conventional investment casting. Furthermore, the heat released during  
cooling of the bulk solidifying amorphous alloy is rather gradual and lacks the  
25 sudden heat release from the latent heat of fusion in conventional materials.  
This characteristic also allows both a relatively cooler (with respect to melt  
temperature) investment mold and the ability to quench the investment mold  
down to temperatures below the glass transition temperature of the bulk-  
solidifying amorphous alloy. In short, it has been surprisingly found that the  
30 ability of bulk-solidifying amorphous alloys to retain their fluidity down to  
glass transition temperatures, which are much lower than the casting  
temperatures, allows for the use of quenching of the investment mold in an  
investment casting process.

35 To the extent that the investment shell is heated, it is preferably  
heated up to a suitable temperature under an inert atmosphere and  
preferably in vacuum in order to release any trapped gas and humidity on the

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inner cavity surfaces of investment shell. The effect of such gases becomes  
highly detrimental not only for the surface quality of castings, but in order to  
5 obtain a high cooling rate as such trapped gases can form bubbles and impede  
the heat transfer from the molten metal to the investment shell.

The introduction of the molten alloy into the cavity of the investment  
mold and the filling of the cavities of the investment mold can be carried out  
10 with a variety of methods. A particularly preferred embodiment is where the  
introduction of the molten metal is carried out when the investment mold is  
under vacuum or in-situ pulling of vacuum. The forces used to introduce the  
molten metal can also take several forms such as gravity feeding, centrifugal  
15 forcing, vacuum suction/assist, or external pressure application such as by use  
of inert gas. In one preferred embodiment, the introduction of the molten  
metal is carried out in the form of counter-gravity casting. In another  
embodiment, the introduction of molten metal is carried out by centrifugal  
20 forces.

After the investment cavity is filled, the investment mold is brought  
into contact with a quenching media (Step 5). This can be carried out by  
submerging the investment shell in a fluidized bed or in a liquid bath. After  
25 the initial quenching, the investment can be separated from the cast  
component either by agitation or other means such as mechanical forces  
(Step 6).

The cast metallic components can be retained in the quenching media  
30 or optionally can be transferred into another quenching media to enhance the  
cooling rate in the bulk of the cast component (Step 7). This step is especially  
preferred for casting components of larger dimensions, such as ones with  
outer dimensions of larger than about 30 mm or thicknesses of about 5 mm or  
35 higher.

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Although several new steps are provided in the above method, the investment shell itself can be prepared in accordance with the above mentioned conventional methods utilizing conventional investment materials. However, given the importance of heat transfer to the investment casting of bulk-solidifying amorphous alloys, in one preferred embodiment, the thickness of the investment shell is desired to be less than about 5.0 mm and more preferably less than about 3.0 mm. For smaller casting parts, with outer dimensions less than about 10 mm, still thinner investment shells of less than about 2.0 mm, can be utilized. These thin walls help speed the rather progressive heat release during solidification of bulk-solidifying amorphous alloys (unlike conventional crystalline metals, which release heat of fusion rather fast during a narrow temperature window).

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Although any suitable casting mold design may be used, it should be noted that some part geometries are particularly preferred for investment casting of bulk-solidifying amorphous alloys. Particularly preferred are part geometries for hollow objects, and geometries of high aspect ratios. These geometries can be defined by the following "defining ratio":

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Defining Ratio = outer dimension:thickness

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For example, for hollow objects, the ratio of outer dimension to the thickness of the part becomes the defining ratio. For example, in the case of a tube-like component, the ratio of the outside diameter (OD) to the wall thickness (t) will be the defining ratio. In another example of a semi-spherical or dome-like component, the diameter of the sphere to the wall thickness becomes the defining ratio. For high-aspect ratio objects, the ratio of the larger dimension to the smallest dimension will be the defining ratio. For example, in the case of a disc-like object, the diameter of the disc to the thickness of the disc will be the defining ratio. It should be understood that the above definitions can be extended and applied to the more complex part

1 geometries in the spirit of the current invention , where typical cross-sections  
of these complex objects can be utilized to reach the defining ratios.

5 In one preferred embodiment, a superheating of about 100 °C above the  
melting temperature is utilized. In another embodiment, a superheating of  
about 200 °C or more superheating is employed To prevent this preferably the  
heating of the bulk amorphous metal is carried under inert atmosphere or  
10 partial vacuum or full vacuum.

In one embodiment, the defining ratio is larger than about 5. In  
another embodiment, the defining ratio can be larger than about 10. In  
another embodiment, the defining ratio can be larger than about 20. In one  
15 preferred embodiment, the defining ratio is larger than about 5 and the outer  
dimension is smaller than about 10 mm. In another preferred embodiment,  
the defining ratio is larger than about 10 and the outer dimension is less than  
about 30 mm. In still another preferred embodiment, the defining ratio is  
20 larger than about 20 and the outer dimension is less than about 60 mm.

Bulk-solidifying amorphous alloys generally have much lower melting  
temperatures than the melting temperatures of its constituents. This is  
especially true when compared to the weighted averages of the constituent  
25 melting temperatures. Although it may be argued that amorphous alloys do  
not experience a melting phenomenon in the same manner as a crystalline  
material, it is convenient to describe a "melting point" at which the viscosity  
of the material is so low that, to the observer, it behaves as a melted solid.  
30 The melting point or melting temperature of the amorphous metal may be  
considered as the temperature at which the viscosity of the material falls  
below about  $10^2$  poise. Alternatively, the melting temperature of the  
crystalline phases of the bulk-solidifying amorphous alloy composition can be  
35 taken as the melting temperature of the amorphous alloy. For example Zr-Ti  
based bulk-solidifying amorphous alloys typically have melting temperatures  
of about 800 ° C or less.

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Although any suitable bulk-solidifying amorphous alloys can be utilized in one or another form of the invention, ones with lower critical cooling rates are preferred. In one preferred embodiment of the invention, a bulk-solidifying amorphous alloy with a critical cooling rate of less than about 50 °C/sec is used. In a still more preferred embodiment of the invention, a bulk-solidifying amorphous alloy with a critical cooling rate of less than about 5 °C/sec is used. A particularly preferred characteristic of the bulk-solidifying amorphous alloy is the enhanced stability against crystallization at temperatures above the glass transition temperature,  $T_g$ , but at temperatures substantially below the melting temperature. This characteristic can be defined by  $\Delta T_{sc}$  ( $\Delta T$ -super-cooled liquid region is defined as the difference of  $T_x$  and  $T_{sc}$ , as shown in FIG. 4). The bulk-solidifying amorphous alloy in accordance with the current invention preferably has a  $\Delta T_{sc}$  (supercooled liquid region) of more than about 30 °C, and preferably a  $\Delta T_{sc}$  of more than about 60 °C, and still most preferably a  $\Delta T_{sc}$  of about 90 °C or more.

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For the purposes of this disclosure,  $T_g$ ,  $T_{sc}$  and  $T_x$  are determined from standard DSC (Differential Scanning Calorimetry) scans at 20 °C.  $T_g$  is defined as the onset temperature of glass transition,  $T_{sc}$  is defined as the onset temperature of super-cooled liquid region, and  $T_x$  is defined as the onset temperature of crystallization.  $\Delta T_{sc}$  is defined as the difference between  $T_x$  and  $T_{sc}$ . All the temperature units are in °C. A diagram of a typical phase transition curve for an exemplary bulk-solidifying amorphous alloy is shown in FIG. 4.

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A high value of  $\Delta T_{sc}$  becomes crucial as the effective cooling rate of the molten metal in such a disclosed investment casting process decreases rather more dramatically at temperatures substantially below the melting temperatures than generally experienced in typical metallic mold casting process.

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5 A particularly preferred bulk-solidifying amorphous alloy composition is one having a single crystallization in a smaller temperature range and at a high peak transformation rate in a typical DSC heating scan.

10 In a typical DSC heating scan of bulk solidifying amorphous alloys, crystallization can take in one or more steps. The preferred bulk-solidifying amorphous alloys are ones with a single crystallization step in a typical DSC heating scan. However, most of the bulk solidifying amorphous alloys crystallize in more than one step in a typical DSC heating scan. (For the purposes of this disclosure all the DSC heating scans are carried out at the rate of 20 °C/min and all the extracted values are from DSC scans at 20 °C/min. Other heating rates such as 40 °C/min, or 10 °C/min can also be utilized while basic physics of this disclosure still remaining intact).

20 Shown schematically in FIG. 5 is one type of crystallization behavior of a bulk-solidifying amorphous alloy in a typical DSC scan such as at 20° C/min heating rate. The crystallization happens to occur over in two steps. The first crystallization step occurs over a relatively large temperature range at a relatively slower peak transformation rate, whereas the second crystallization occurs over a smaller temperature range than the first one and at a much faster peak transformation rate than the first one. Here  $\Delta T1$  and  $\Delta T2$  are defined as the temperature ranges over which the first and second crystallization steps proceed, respectively.  $\Delta T1$  and  $\Delta T2$  can be calculated by taking the difference between the onset of the crystallization and “outset” of the crystallization which are calculated in a similar manner for  $T_x$  by taking the cross section point of preceding and following trend lines as depicted in FIG 5. The enthalpy of crystallization  $\Delta H1$  and  $\Delta H2$  can then be calculated by calculating the peak heat flow value compared to the baseline heat flow. (It should be noted that although the absolute values of  $\Delta T1$ ,  $\Delta T2$ ,  $\Delta H1$  and  $\Delta H2$  depend on the specific DSC set-up and the size of the test specimens used, the relative scaling (i.e.  $\Delta T1$  vs  $\Delta T2$ ) should remain intact).



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Shown schematically in FIG. 6 is another type of crystallization behavior of a bulk-solidifying amorphous alloy in a typical DSC scan such as at a heating rate of 20° C/min. In this figures, the crystallization again occurs in two steps, however, the first crystallization step occurs over a relatively small temperature range at a relatively faster peak transformation rate, whereas the second crystallization occurs over a larger temperature range than the first one and at a much slower peak transformation rate than the first one. Here  $\Delta T1$ ,  $\Delta T2$ ,  $\Delta H1$  and  $\Delta H2$  are defined and calculated as above.

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It should be noted that although, only two crystallization steps are shown above, the crystallization behavior of some bulk solidifying amorphous alloys can take place in more than two steps. In such cases, the subsequent  $\Delta T3$ ,  $\Delta T4$  ... and  $\Delta H3$ ,  $\Delta H4$  ... can also be defined. In such cases, the preferred compositions of bulk amorphous alloys are ones where  $\Delta H1$  is the largest of  $\Delta H1$ ,  $\Delta H2$ , ... $\Delta HN$ .

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In all such cases, a sharpness ratio can be defined for each crystallization step by  $\Delta HN / \Delta TN$ . The higher  $\Delta H1 / \Delta T1$  compared to the other  $\Delta HN / \Delta TN$ , the more preferred the alloy composition. Thus, for the two cases discussed above, the bulk-solidifying amorphous alloy with the second crystallization behavior (FIG. 6) is the preferred alloy for investment casting, and especially with larger section thickness.

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Accordingly, from a given family of bulk solidifying amorphous alloys, the preferred composition is with the highest  $\Delta H1 / \Delta T1$  compared to other crystallization steps. For example, a preferred alloy composition has  $\Delta H1 / \Delta T1 > 2.0 * \Delta H2 / \Delta T2$ . Still more preferable is  $\Delta H1 / \Delta T1 > 4.0 * \Delta H2 / \Delta T2$ .

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Although specific embodiments are disclosed herein, it is expected that persons skilled in the art can and will design alternative investment casting methods that are within the scope of the following description either literally or under the Doctrine of Equivalents.